第93108775號初審引證附件3

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 619 325 A1**

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number: 93870064.8

(51) Int. Cl.5: C08F 4/602, C08F 10/00

(22) Date of filing: 07.04.93

(43) Date of publication of application: 12.10.94 Bulletin 94/41

(84) Designated Contracting States: AT BE CH DE DK ES FR GB GR IE IT LI LU MC NL PT SE

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(54) **Catalyst and process for producing polyolefins.**

(57) The present invention provides a process for preparing polyolefins having a multimodal or at least bimodal molecular weight distribution by contacting in a reaction mixture under polymerization conditions at least one olefin and a catalyst system comprising a supported catalyst-component comprising an alumoxane and at least two metallocenes containing the same transition metal and selected from mono, di, and tri-cyclopentadienyls and substituted cyclopentadienyls of a transition metal and wherein at least one of the metallocenes is bridged and at least one of the metallocenes is unbridged.

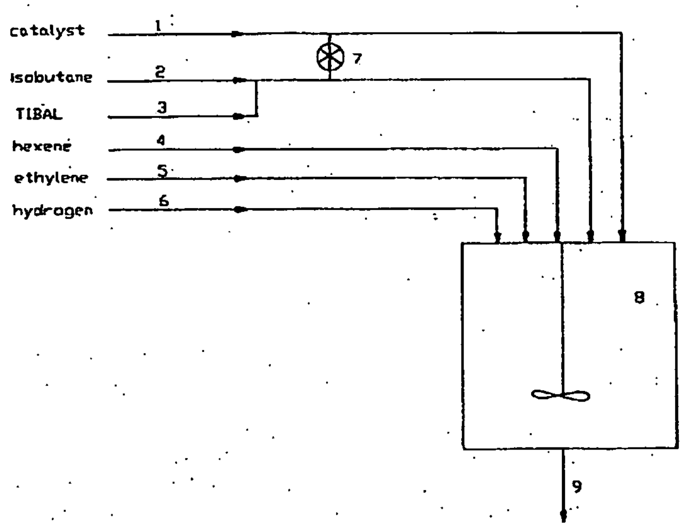

FIG. 1

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This invention relates to a method for preparing polyolefins having a bi- or multimodal molecular weight distribution. This invention also relates to a polyolefin polymerization catalyst system. This invention further relates to a method for preparing an olefin polymerization catalyst system.

Polyolefins having a multimodal molecular weight distribution (MWD) can be converted into articles by extrusion molding, thermoforming, rotational molding, etc. and have advantages over typical polyolefins lacking the multimodal MWD. Polyolefins having a multimodal MWD may be processed more easily, i .e. they can be processed at a faster throughput rate with lower energy requirements and at the same time such polymers evidence reduced melt flow perturbations and are preferred due to improved properties for applications such as high strength films.

There are several known methods for producing polyolefins having a multimodal MWD; however, each method has its own disadvantages. Polyolefins having a multimodal MWD can be made by employing two distinct and separate catalysts in the same reactor each producing a polyolefin having a different MWD; however, catalyst feed rate is difficult to control and the polymer particles produced are not uniform in size, thus, segregation of the polymer during storage and transfer can produce non-homogeneous products. A polyolefin having a bimodal MWD can also be made by sequential polymerization in two separate reactors or by blending polymers of different MWD during processing; however, both of these methods increase capital cost.

European Patent N° 0128045 discloses a method of producing polyethylene having a broad molecular weight distribution and/or a multimodal MWD. The polyethylenes are obtained directly from a single polymerization process in the presence of a catalyst system comprising two or more metallocenes each having different propagation and termination rate constants, and aluminoxane.

There are certain limits to the known methods for preparing bimodal molecular weight distribution or multimodal molecular weight distribution polyolefins. Even under ideal conditions the gel permeation chromatograph curves don't show a marked bimodal MWD of the polyolefin. The MWD and shear rate ratios of the polymer and the catalyst activity disclosed in the known methods are rather poor. Further the known metallocene catalyst systems for producing bimodal MWD use aluminoxane as cocatalyst during the polymerization which causes severe fouling inside the reactor and renders the use of such a type of catalyst in continuous processes almost impossible.

It is therefore not surprising that none of the known methods for producing a multimodal MWD polyolefin from a single polymerization process in the presence of a catalytic system comprising at least two metallocenes have been developed at an industrial scale.

It is an object of the present invention to provide for a new process for preparing polyolefins having a multimodal molecular weight distribution. It is an object of the present invention to provide a new high activity polymerization catalyst system. It is a further object of the present invention to provide for a new process for preparing the polymerization catalyst system of the present invention.

In accordance with the present invention, polyolefins having a multimodal or at least bimodal molecular weight distribution are prepared by contacting in a reaction mixture under polymerization conditions at least one olefin , a catalyst system comprising (a) a supported catalyst-component comprising an alumoxane and at least two metallocenes containing the same transition metal and selected from mono, di, and tri-cyclopentadienyls and substituted cyclopentadienyls of a transition metal wherein at least one of the metallocenes is bridged and at least one of the metallocenes is unbridged and (b) a cocatalyst.

While alumoxane can be used as cocatalyst, the Applicant has found that it was not necessary to use alumoxane as cocatalyst during the polymerization procedure for preparing polyolefins according to the process of the present Invention. Further the use of alumoxane as a cocatalyst during the polymerization may lead to the fouling of the reactor.

According to a preferred embodiment of the present invention, one or more cocatalysts represented by the formula MR_x are used, wherein M is a metal selected from Al, B, Zn, Li and Mg, each R is the same or different and is selected from halides or from alkoxy or alkyl groups having from 1 to 12 carbon atoms and x is from 1 to 3. Especially suitable cocatalysts are trialkylaluminium selected from trimethylaluminium, triethylaluminium, triisobutylaluminium, tri-n-hexylaluminium or tri-n-octylaluminium, the most preferred being triisobutylaluminium.

In accordance with the present invention the broadness of the molecular weight distribution and the average molecular weights can be controlled by selecting the catalyst system. In a preferred embodiment of the present invention, this control is also performed by the introduction of some amount of hydrogen during polymerization. Another preferred embodiment of the present invention implies the use of a comonomer for this control ; examples of comonomer which can be used include 1-olefins such as 1-butene, 1-hexene, 1-octene, 4-methyl-pentene, and the like, the most preferred being 1-hexene.

It has unexpectedly been found that the polymerization process can be conducted under slurry phase polymerization conditions and this constitutes a real advantage of the process of the present invention. While slurry phase polymerization may be conducted under well known operating conditions, it is preferred that it is operated at a temperature of about 20 to 125 °C and a pressure of about 0.1 to 5.6 MPa for a time between 10 minutes and 4 hours.

Another advantage of the present invention is that a continuous reactor can be used for conducting the polymerization. This continuous reactor is preferably a loop reactor. During the polymerization process, the olefin monomer(s), the catalytic system, the cocatalyst and a diluent are flowed in admixture through the reactor.

A further advantage of the present invention is that the bulk density of the polymer obtained by the process of the present invention is particularly high. The bulk density is an important characteristic of the polymer. The bulk density, commonly expressed in terms of grams per cubic centimeters, should be relatively high.

If the bulk density is too low, the polymer will tend to be fluffy and will tend to cause plugging and handling problems in the product transfer system. Low bulk densities mean problems for fluff packaging and for the extrusion processing. This is particularly important in a continuous or a semi-continuous polymerization where plugging of the withdrawal outlet or another point in the polymerization system can cause serious interruptions in production schedules.

According to the present invention when hydrogen is used it is preferred that the relative amounts of hydrogen and olefin introduced into the polymerization reactor be within the range of about 0.001 to 15 mole percent hydrogen and 99.999 to 85 mole percent olefin based on total hydrogen and olefins present, preferably about 0.2 to 3 mole percent hydrogen and 99.8 to 97 mole percent olefin.

It is preferred that the polymerization reaction be run in a diluent at a temperature at which the polymer remains as a suspended solid in the diluent. Diluents include, for examples, isobutane, n-hexane, n-heptane, methylcyclohexane, n-pentane, n-butane, n-decane, cyclohexane and the like. The preferred diluent is isobutane.

The olefin monomer used in the process of the present invention to produce a polyolefin of bimodal or multimodal molecular weight distribution in which each polymer particle contains both high and low molecular weight polymer molecules is preferably selected from ethylene and mono-1-olefins (alpha olefins), preferably mono-1-olefins having from 2 to 10 carbon atoms including for example, 4-methyl-1-pentene. More preferably these mono-1-olefins are selected from the group consisting of ethylene, propylene, and mixtures thereof; ethylene being the most preferred.

According to the present invention, the supported catalyst-component used in the process for producing polyolefins having multimodal molecular weight distribution can be made by any known method as long as it comprises an alumoxane and at least two metallocenes containing the same transition metal wherein at least one of the metallocenes is bridged and at least one of the metallocenes is unbridged.

Known processes of producing these types of catalysts are disclosed in European Patent N° 0206794, the content of which is incorporated by reference.

This patent discloses a catalyst-component comprising the reaction product of at least one metallocene and alumoxane in the presence of a support material thereby providing a supported metallocene-alumoxane reaction product as the sole catalyst component.

The metallocenes used in the process of the present invention are organometallic coordination compounds which are cyclopentadienyl derivatives of a Group 4b, 5b or 6b metal of the Periodic Table and include mono, di and tricyclopentadienyls and their derivatives of the transition metals. Particularly desirable are the metallocene of a Group 4b and 5b metal such as titanium, zirconium, hafnium and vanadium.

The preferred metallocenes can be represented by the general formulae:

I. $(Cp)_m MR_nX_q$

wherein Cp is a cyclopentadienyl ring, M is a Group 4b, 5b or 6b transition metal, R is a hydrocarbyl group or hydrocarboxy having from 1 to 20 carbon atoms, X is a halogen, and m = 1-3, n = 0-3, q = 0-3 and the sum of m+n+q will be equal to the oxidation state of the metal.

II. $(C_5R'_k)_gR''_s(C_5R'_k)MQ_{3-g}$

and

III. $R''_s(C_5R'_k)_2MQ'$

wherein $(C_5R'_k)$ is a cyclopentadienyl or substituted cyclopentadienyl, each R' is the same or different and is hydrogen or a hydrocarbyl radical such as alkyl, alkenyl, aryl, alkylaryl, or arylalkyl radical containing from 1 to 20 carbon atoms or two carbon atoms are joinded together to form a C_4-C_6 ring, R" is a C_1-C_4 alkylene radical, a dialkyl germanium or silicon or siloxane, or a alkyl phosphine or amine radical bridging two $(C_5R'_k)$ rings, Q is a hydrocarbyl radical such as aryl, alkyl, alkenyl, alkylaryl, or aryl alkyl radical having from 1-20 carbon atoms, hydrocarboxy radical having 1-20 carbon atoms or halogen and can be the same or different from each other, Q' is an alkylidiene radical having from 1 to about 20 carbon atoms, s is 0 or 1, g is 0, 1 or 2, s is 0 when g is 0, k is 4 when s is 1 and k is 5 when s is 0, and M is as defined above.

Exemplary hydrocarbyl radicals are methyl, ethyl, propyl, butyl, amyl, isoamyl, hexyl, isobutyl, heptyl, octyl, nonyl, decyl, cetyl, 2-ethylhexyl, phenyl and the like.

Exemplary halogen atoms include chlorine, bromine, fluorine and iodine and of these halogen atoms, chlorine is preferred.

Exemplary hydrocarboxy radicals are methoxy, ethoxy, propoxy, butoxy, amyloxy and the like.

Exemplary of the alkylidiene radicals is methylidene, ethylidene and propylidene.

According to a preferred embodiment of the present invention, the catalyst-component comprises at least two metallocenes deposited on a support wherein :

- at least one of the metallocenes is unbridged and is represented by the formula $(Cp)_2MX_2$ wherein each Cp is the same or different and is selected from substituted or unsubstituted cyclopentadienyl, indenyl or fluorenyl, M is zirconium, titanium or hafnium and X, which is the same or different, is a hydrocarbyl radical such as aryl, alkyl, alkenyl, alkylaryl, or aryl alkyl radical having from 1-20 carbon atoms or a halogen.
- at least one of the metallocenes is bridged and is represented by the formula $R''(Cp)_2MX_2$ wherein each Cp is the same or different and is selected from substituted or unsubstituted cyclopentadienyl, indenyl or fluorenyl, M is zirconium, titanium or hafnium, X, which is the same or different, is a hydrocarbyl radical such as aryl, alkyl, alkenyl, alkylaryl, or aryl alkyl radical having from 1-20 carbon atoms or a halogen and R" is a C_1-C_4 alkylene radical, a dialkyl germanium or silicon or siloxane, or a alkyl phosphine or amine radical bridging two (Cp) rings.

Preferably, in the above-identified formulae, for the unbridged metallocene Cp is a substituted or unsubstituted cyclopentadienyl or indenyl, M is zirconium, titanium or hafnium and X is Cl or CH_3, and for the bridged metallocene Cp is a substituted or unsubstituted cyclopentadienyl, indenyl or fluorenyl, M is zirconium, titanium or hafnium, X is Cl or CN_3 and R" is an ethylene radical or silicon.

Preferably, the unbridged metallocene is a bis(cyclopentadienyl) zirconium dichloride and the bridged metallocene is an ethylene-bis(indenyl) zirconium dichloride.

The molar ratio of the unbridged metallocenes to the bridged metallocenes can vary over a wide range, and in accordance with the present invention, the only limitation on the molar ratio is the breadth of the molecular weight distribution (MWD) and the degree of bimodality desired in the product polymer. Preferably, the unbridged to bridged metallocenes molar ratio will be between 10:1 and 1:10, preferably between 5:1 and 1:5, more preferably between 4:1 and 2:1.

The alumoxanes used in the process of the present invention are well known and preferably comprise oligomeric linear and/or cyclic alkyl alumoxanes represented by the formula :

$$\text{(I)}\quad R-(\underset{R}{Al}-O)_n-AlR_2$$

for oligomeric, linear alumoxanes and

$$\text{(II)}\quad (-\underset{R}{Al}-O-)_m$$

for oligomeric, cyclic alumoxane,

wherein n is 1-40, preferably 10-20, m is 3-40, preferably 3-20 and R is a C_1-C_8 alkyl group and preferably methyl. Generally, in the preparation of alumoxanes from, for example, aluminum trimethyl and water, a mixture of linear and cyclic compounds is obtained.

The support used in the process of the present invention can be any of the solid, particularly, porous supports such as talc, inorganic oxides, and resinous support materials such as polyolefin.
Preferably, the support material is an inorganic oxide in its finely divided form.
Suitable inorganic oxide materials which are desirably employed in accordance with this invention include Group 2a, 3a, 4a or 4b metal oxides such as silica, alumina and mixtures thereof. Other inorganic oxides that may be employed either alone or in combination with the silica, or alumina are magnesia, titania, zirconia, and the like. Other suitable support materials, however, can be employed, for example, finely divided functionalized polyolefins such as finely divided polyethylene.
Preferably, the support is a silica having a surface area comprised between 200 and 600 m^2/g and a pore volume comprised between 0.5 and 3 ml/g.

The amount of alumoxane and metallocenes usefully employed in the preparation of the solid support catalyst can vary over a wide range. Preferably the aluminium to transition metal mole ratio is comprised between 1:1 and 100:1, preferably between 5:1 and 50:1.

The order of addition of the metallocenes and alumoxane to the support material can vary. In accordance with a preferred embodiment of the present invention alumoxane dissolved in a suitable inert hydrocarbon solvent is added to the support material slurried in the same or other suitable hydrocarbon liquid and thereafter a mixture of the at least two metallocenes is added to the slurry.

According to a preferred embodiment of the present invention, the supported catalyst-component is prepared by mixing together the unbridged metallocene alumoxane supported catalyst with the bridged metallocene alumoxane supported catalyst.

Preferred solvents include mineral oils and the various hydrocarbons which are liquid at reaction temperatures and which do not react with the individual ingredients. Illustrative examples of the useful solvents include the alkanes such as pentane, iso-pentane, hexane, heptane, octane and nonane; cycloalkanes such as cyclopentane and cyclohexane, and aromatics such as benzene, toluene, ethylbenzene and diethylbenzene.
Preferably the support material is slurried in toluene and the metallocene and alumoxane are dissolved in toluene prior to addition to the support material .

Examples

1. Catalyst preparation (A)

The support used is a silica having a surface area of 322 m^2/g (GRACE 952). This silica is further prepared by drying in high vacuum on a schlenk line for three hours to remove the physically absorbed water and then suspended in toluene to react with methyl alumoxane (MAO) for three hours at the reflux temperature. Finally it is cooled and washed tree times with toluene to remove the unreacted MAO. A solution of the two corresponding metallocenes in toluene is added to the treated silica and the mixture is stirred for an hour. The supernatant liquid was filtered off and the remaining solid was dried under vacuum after being washed three times with toluene. Three minutes before the introduction of the catalyst into the reaction zone 1 ml of 25wt% of triisobutylaluminium (TIBAL) in toluene is added. All polymerizations were performed in a two liter Buchi reactor in one liter of iso-butane as diluent.

2. Polymerization procedure (A)

A suspension of supported catalyst is introduced into the reactor under the iso-butane pressure. The polymerization is initiated by pressurizing the reactor with 30 bars of ethylene. The ethylene pressure is maintained during the whole duration of the polymerization. The polymerization is stopped by cooling the reactor and venting the ethylene. The polymer is recovered and analyzed. The catalyst type, the polymerization conditions and the polymer properties are given in table 1.

3. Catalyst preparation (B)

The two supports used are MAO supported silica identical to the one prepared in method (A) hereabove.
(a) a solution of $(Cp)_2ZrCl_2$ in toluene is deposited on the first support by stirring the resulting suspension for one hour at ambient temperature. The supernatant liquid was filtered off and the remaining solid was dried under vacuum after being washed three times with toluene.

(b) a solution of $(Ind)_2ZrCl_2$ in toluene is deposited on the second support by stirring the resulting suspension for one hour at ambient temperature. The supernatant liquid was filtered off and the remaining solid was dried under vacuum after being washed three times with toluene.

(c) the two separately obtained supported metallocenes (a) and (b) were mixed together in a 2:1 weight ratio ((a):(b)).

4. Polymerization procedure (B)

The reactor used in all examples has a capacity of 35 liters and is continuously agitated. This continuous reactor is first filled with isobutane at a pressure of 40 bars. Then, as indicated in figure 1, a suspension of supported catalyst (1), isobutane (2), TIBAL (3), hexene (4), ethylene (5) and hydrogen (6) are continuously introduced into the reactor. The polymers are recovered at (9). All polymers were analyzed by Gel Permeation Chromatography (GPC-WATERS MILLIPORE) and Differential Scanning Calorimetry (DSC). The graphs are given in figures 2 to 20 (figures 2 to 20 respectively correspond to examples 5 to 23 of table 2). "D" represents the ratio Mw/Mn (MWD), "D'" the ratio Mz/Mw and "A" the area under the curve. The polymerization conditions and the polymer properties are given in table 2.

TABLE 1

Example	Catalyst (mg)	type	Hexene (ml)	Hydrogen (Nl)	Yield (g)	Activity (g/g.h)	Bulk (1) (g/cc)	MI_2 (2) (g/10')	HLMI (3) (g/10')	SRR (4)
1	52 99	(B) (A)	10	4.5	100	1025	0.3	(a)	(a)	(b)
2	50 100	(B) (A)	10	1	135	1126	0.27	1.15	49.5	43.04
3(x)	50 100	(B) (A)	10	2.5	120	946	0.3	0.61	23.9	39.18
4	50 100	(B) (A)	5	1	170	662	0.25	0.58	22.3	38.44

(A) bis(cyclopentadienyl) zirconium dichloride
(B) ethylene-bis(indenyl) zirconium dichloride
(x) precontact time of 45 minutes between catalyst and cocatalyst before polymerization
(1) Bulk Density (ASTM-D-1895)
(2) Melt Index (ASTM-D-1238-89A)
(3) High Load Melt Index (ASTM-D-1238-89A)
(4) Shear Rate Response ($HLMI/MI_2$)
(a) too high to be measured
(b) non determined

TABLE 1 (continued)

Example	Catalyst (mg)	Catalyst type	Density (1) (g/cc)	Mz x10E3	Mw x10E3	Mn x10E3	MWD	MP (2) (°C)	H (3) (J/g)
1	52 99	(B) (A)	(b)	(b)	(b)	(b)	(b)	127.8	192
2	50 100	(B) (A)	0.9521	(b)	(b)	(b)	(b)	131	180
3(x)	50 100	(B) (A)	0.9518	1100	137	12	11	132.3	189.5
4	50 100	(B) (A)	0.9408	1230	132	15.5	8.5	133	191.2

(A) bis(cyclopentadienyl) zirconium dichloride
(B) ethylene-bis(indenyl) zirconium dichloride
(x) precontact time of 45 minutes between catalyst and cocatalyst before polymerization
(1) ASTM-D-1505-85
(2) Melting Point (DSC)
(3) Enthalpy of fusion (DSC)
(b) non determined

TABLE 2

Ex	Cata (g/h)	TIBAL (g/h)	i-C_4 (kg/h)	C_2 (kg/h)	C_6 (cc/h)	H_2 (Nl/h)	Bulk (1) (g/cc)	MI_2 (2) (g/10')	HLMI (3) (g/10')	SRR (4)	D (5) (g/cc)	Mz x10E3	Mw x10E3	Mn x10E3	MWD
5	4.5	7.2	18	3	0	33	0.38	0.22	45.9	204	0.965	2218	254	7.7	33.0
6	4.5	7.2	18	2.5	0	14	0.37	0.12	30.6	251	0.963	2492	300	9.0	33.3
7	4.5	7.2	18	2.5	0	15	0.37	0.05	13.9	259	0.965	2699	357	10.2	35.0
8	4.5	7.2	18	2.5	0	15	0.35	0.05	13.6	300	0.964	2868	381	10.2	37.4
9	4.5	7.2	16	2	268	15	0.38	0.07	15.7	225	0.958	2644	337	9.4	35.7
10	4.5	7.2	16	2	265	15	0.39	0.09	23.9	266	0.959	2486	323	9.4	34.5
11	4.5	7.2	16	2	270	15	0.39	0.08	24.0	312	0.958	2390	307	9.0	34.1
12	4.5	7.2	16	2	274	15	0.39	0.11	24.8	232	0.958	2402	308	9.1	33.8
13	4.5	7.2	16	2	268	15	0.39	0.10	24.5	255	0.959	2437	325	9.7	33.6

Catalyst preparation (B)
(1) Bulk Density (ASTM-D-1895)
(2) Melt Index (ASTM-D-1238-89A)
(3) High Load Melt Index (ASTM-D-1238-89A)
(4) Shear Rate Response (HLMI/MI_2)
(5) Density (ASTM-D-1505-85)
TIBAL triisobutylaluminium, i-C_4 isobutane, C_2 ethylene, C_6 hexene

TABLE 2 (continued)

Ex	Cata (g/h)	TIBAL (g/h)	i-C_4 (kg/h)	C_2 (kg/h)	C_6 (cc/h)	H_2 (Nl/h)	Bulk (1) (g/cc)	MI_2 (2) (g/10')	HLMI (3) (g/10')	SRR (4)	D (5) (g/cc)	Mz x10E3	Mw x10E3	Mn x10E3	MWD
14	4.5	7.2	18	2	0	0	0.30	0.16	11.8	74	0.951	2068	216	19.3	11.2
15	4.5	7.2	18	2	0	0	0.28	0.08	6.5	80	0.951	2569	264	26.3	10.0
16	4.5	7.2	18	2	0	0	0.28	0.14	9.6	69	0.951	1751	198	18.7	10.6
17	4.5	7.2	18	2.5	198	0	0.30	0.09	7.4	80	0.945	2419	270	27.0	10.0
18	4.5	7.2	18	2.5	200	0	0.30	0.07	6.1	94	0.941	2498	282	29.0	9.7
19	4.5	7.2	18	2.5	205	0	0.30	0.05	5.6	110	0.941	2488	288	30.1	9.6
20	4.5	7.2	18	2.5	207	0	0.30	0.05	5.1	97	0.939	2257	270	32.0	8.4
21	4.5	7.2	16	2	202	10	0.30	0.13	11.4	87	0.945	2341	250	18.3	13.7
22	4.5	7.2	16	2	210	10	0.30	0.11	9.1	78	0.946	2653	261	19.0	13.8
23	4.5	7.2	16	2	200	12	0.29	0.10	7.9	78	0.942	2162	247	23.6	10.5

Catalyst preparation (B)
(1) Bulk Density (ASTM-D-1895)
(2) Melt Index (ASTM-D-1238-89A)
(3) High Load Melt Index (ASTM-D-1238-89A)
(4) Shear Rate Ratio ($HLMI/MI_2$)
(5) Density (ASTM-D-1505-85)
TIBAL triisobutylaluminium, i-C_4 isobutane, C_2 ethylene, C_6 hexene

Claims

1. A catalyst system for use in the preparation of polyolefins having a multimodal or at least bimodal molecular weight distribution comprising a supported catalyst-component comprising an alumoxane and

at least two metallocenes containing the same transition metal and selected from mono, di, and tri-cyclopentadienyls and substituted cyclopentadienyls of a transition metal wherein at least one of the metallocenes is bridged and at least one of the metallocenes is unbridged.

2. A catalyst system according to claim 1 further comprising one or more cocatalysts represented by the formula MR_x, wherein M is a metal selected from Al, B, Zn, Li and Mg, each R is the same or different and is selected from halides or from alkoxy or alkyl groups having from 1 to 12 carbon atoms and x is from 1 to 3.

3. A catalyst system according to claim 2 wherein the cocatalyst is a trialkylaluminium selected from trimethylaluminium, triethylaluminium triisobutylaluminium, tri-n-hexylaluminium or tri-n-octylaluminium, preferably triisobutylaluminium.

4. A catalyst system according to anyone of the preceding claims wherein :
   - the unbridged metallocenes are represented by the formula $(C_p)_2MX_2$ wherein each C_p is the same or different and is selected from substituted or unsubstituted cyclopentadienyl, indenyl or fluorenyl, M is zirconium, titanium or hafnium and X, which is the same or different, is a hydrocarbyl radical such as aryl, alkyl, alkenyl, alkylaryl, or aryl alkyl radical having from 1-20 carbon atoms or a halogen.
   - the bridged metallocenes are represented by the formula $R''(C_p)_2MX_2$ wherein each C_p is the same or different and is selected from substituted or unsubstituted cyclopentadienyl, indenyl or fluorenyl, M is zirconium, titanium or hafnium and X, which is the same or different, is a hydrocarbyl radical such as aryl, alkyl, alkenyl, alkylaryl, or aryl alkyl radical having from 1-20 carbon atoms or a halogen and R" is a C_1-C_4 alkylene radical, a dialkyl germanium or silicon or siloxane, or a alkyl phosphine or amine radical bridging two (C_p) rings.

5. A catalyst system according to claim 4 wherein in the formula of the unbridged metallocene Cp is a substituted or unsubstituted cyclopentadienyl or indenyl, M is zirconium, titanium or hafnium and X is Cl or CH_3, and in the formula of the bridged metallocene Cp is a substituted or unsubstituted cyclopentadienyl, indenyl or fluorenyl, M is zirconium, titanium or hafnium, X is Cl or CH_3 and R" is an ethylene radical or silicon.

6. A catalyst system according to claim 5 wherein the unbridged metallocene is a bis(cyclopentadienyl) zirconium dichloride and the bridged metallocene is an ethylene-bis(indenyl) zirconium dichloride.

7. Process for the preparation of polyolefins having a multimodal or at least bimodal molecular weight distribution comprising :
   (1) providing a catalyst system comprising (a) a supported catalyst-component comprising an alumoxane and at least two metallocenes containing the same transition metal and selected from mono, di, and tri-cyclopentadienyls and substituted cyclopentadienyls of a transition metal wherein at least one of the metallocenes is bridged and at least one of the metallocenes is unbridged and (b) a cocatalyst.
   (2) contacting said catalyst system in a polymerization reaction zone with at least one olefin and maintaining said reaction zone under polymerization conditions to produce mulimodal or at least bimodal molecular weight distribution polymer of said olefin.

8. Process according to claim 7 wherein the catalyst system comprises one or more cocatalysts represented by the formula MR_x wherein M is a metal selected from Al, B, Zn, Li and Mg, each R is the same or different and is selected from halides or from alkoxy or alkyl groups having from 1 to 12 carbon atoms and x is from 1 to 3.

9. Process according to claim 8 wherein the cocatalyst is a trialkylaluminium selected from trimethylaluminium, triethylaluminium, triisobutylaluminium, tri-n-hexylaluminium or tri-n-octylaluminium, preferably triisobutylaluminium.

10. Process according to any of claims 7 to 9 wherein the polymerization reaction is run in a diluent including isobutane, n-hexane, n-heptane, methylcyclohexane, n-pentane, n-butane, n-decane, and cyclohexane, preferably isobutane.

11. Process according to any of claims 7 to 10 wherein hydrogen is introduced into the polymerization reaction zone in an amount ranging from about 0.001 to 15 mole percent hydrogen based on total hydrogen and olefin present.

12. Process according to any of claims 7 to 11 wherein
- the unbridged metallocenes are represented by the formula $(Cp)_2MX_2$ wherein each Cp is the same or different and is selected from substituted or unsubstituted cyclopentadienyl, indenyl or fluorenyl, M is zirconium, titanium or hafnium and X, which is the same or different, is a hydrocarbyl radical such as aryl, alkyl, alkenyl, alkylaryl, or aryl alkyl radical having from 1-20 carbon atoms or a halogen.
- the bridged metallocenes are represented by the formula $R''(Cp)_2MX_2$ wherein each Cp is the same or different and is selected from substituted or unsubstituted cyclopentadienyl, indenyl or fluorenyl, M is zirconium, titanium or hafnium and X, which is the same or different, is a hydrocarbyl radical such as aryl, alkyl, alkenyl, alkylaryl, or aryl alkyl radical having from 1-20 carbon atoms or a halogen and R" is a C_1-C_4 alkylene radical, a dialkyl germanium or silicon or siloxane, or a alkyl phosphine or amine radical bridging two (Cp) rings.

13. Process according to claim 12 wherein in the formula of the unbridged metallocene Cp is a substituted or unsubstituted cyclopentadienyl or indenyl, M is zirconium, titanium or hafnium and X is Cl or CH_3, and in the formula of the bridged metallocene Cp is a substituted or unsubstituted cyclopentadienyl, indenyl or fluorenyl, M is zirconium, titanium or hafnium, X is Cl or CH_3 and R" is an ethylene radical or silicon.

14. Process according to claim 13 wherein the unbridged metallocene is a bis(cyclopentadienyl) zirconium dichloride and the bridged metallocene is an ethylene-bis(indenyl) zirconium dichloride.

15. Process for preparing a supported catalyst-component for use in the preparation of polyolefins having a multimodal or at least bimodal molecular weight distribution comprising an alumoxane and at least two metallocenes containing the same transition metal and selected from mono, di, and tri-cyclopentadienyls and substituted cyclopentadienyls of a transition metal wherein at least one of the metallocenes is bridged and at least one of the metallocenes is unbridged, characterized by the fact that the supported catalyst-component is obtained by mixing together the unbridged metallocene alumoxane supported catalyst with the bridged metallocene alumoxane supported catalyst.

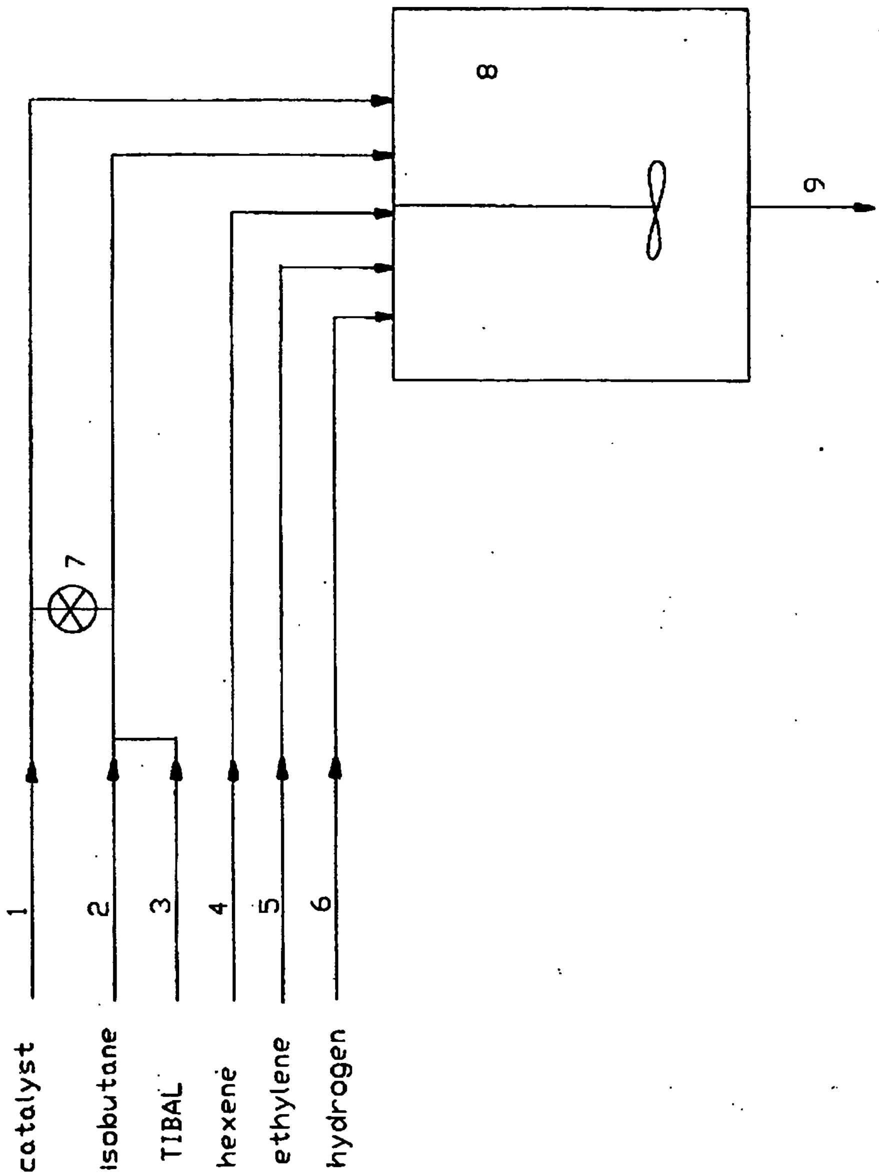
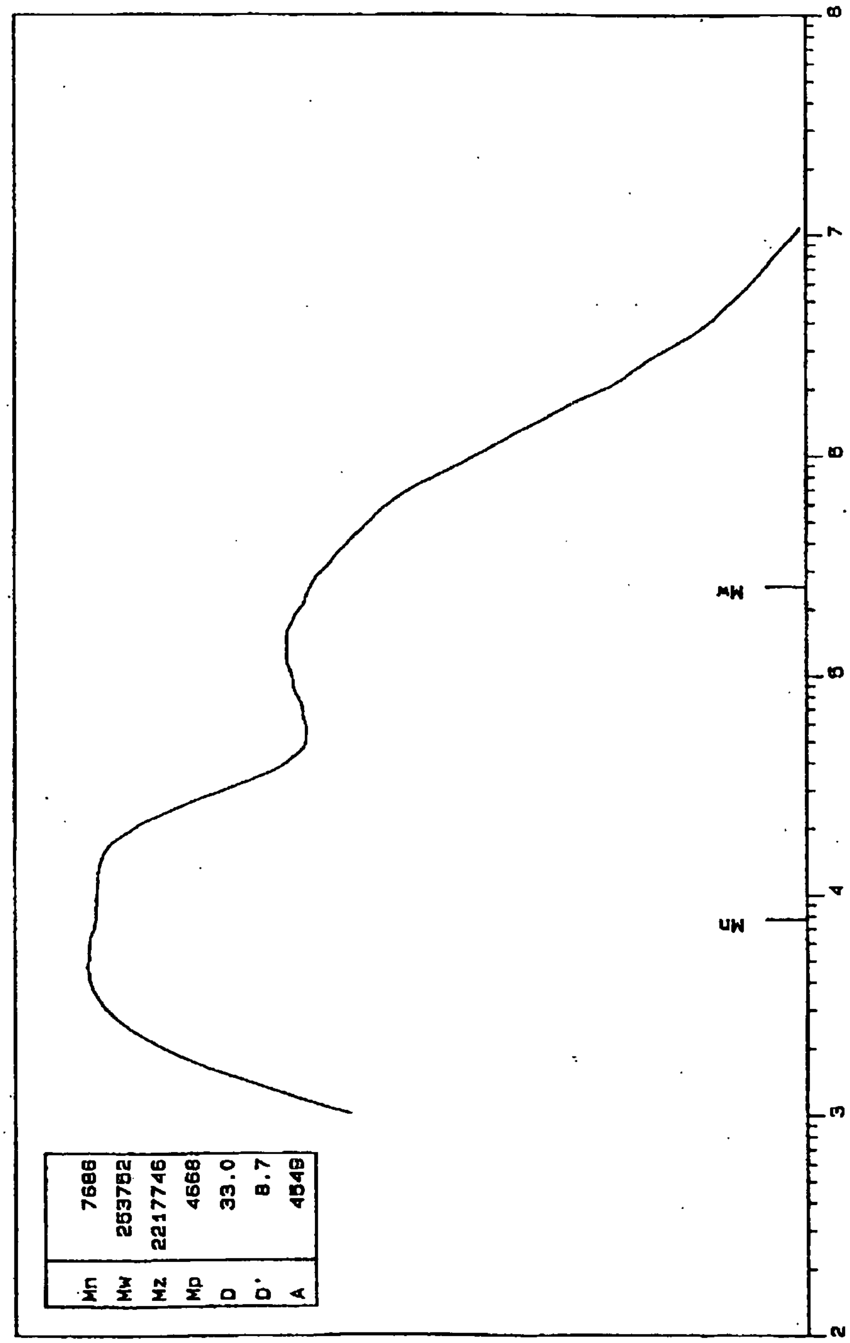

catalyst
isobutane
TIBAL
hexene
ethylene
hydrogen
1
2
3
4
5
6
7
8
9

FIG. 1


Mn 7688
Mw 253752
Mz 2217746
Mp 4668
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D' 8.7
A 4548
Mn
Mw
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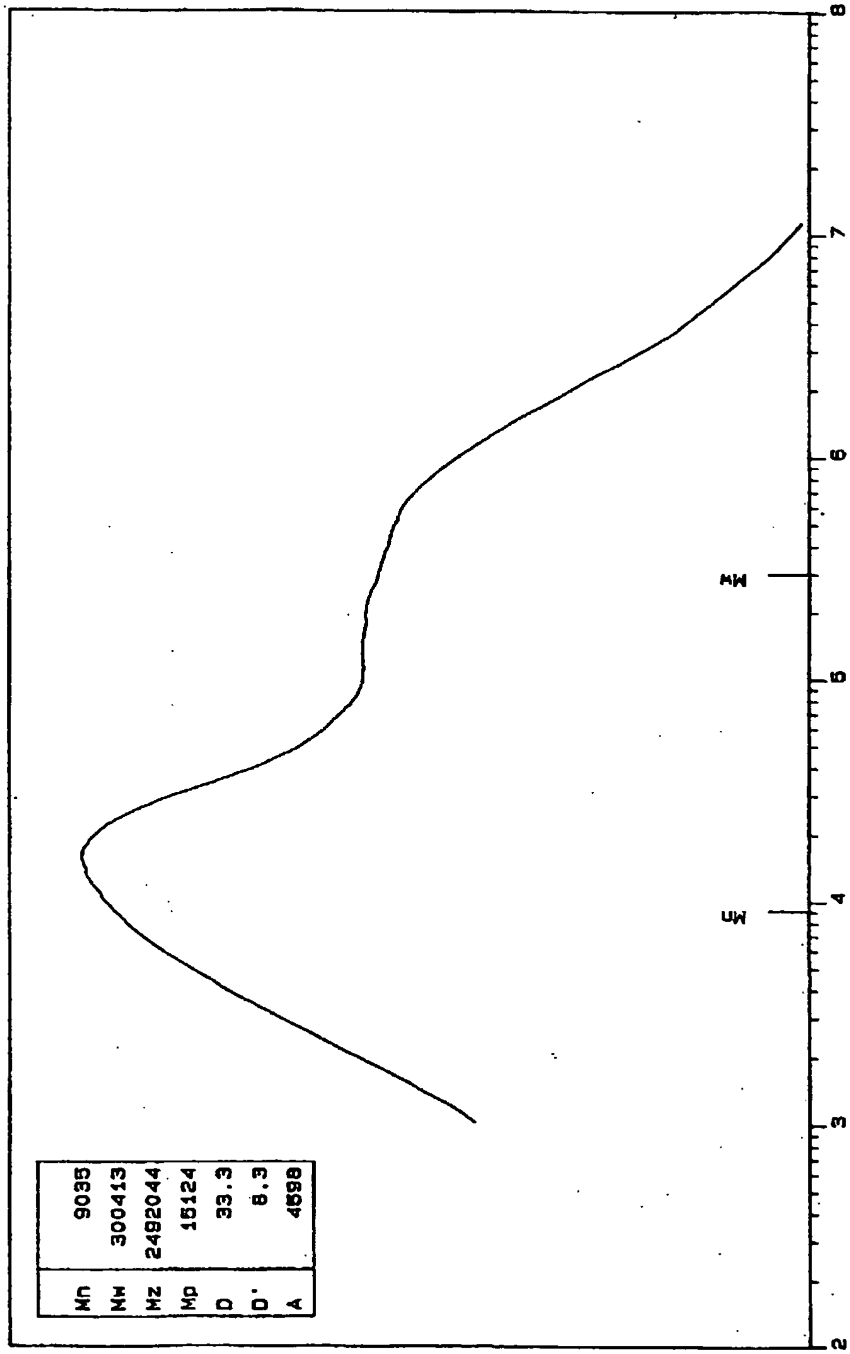
5
6
7
8

FIG.2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Mw 300413
Mz 2492044
Mp 15124
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A 4598
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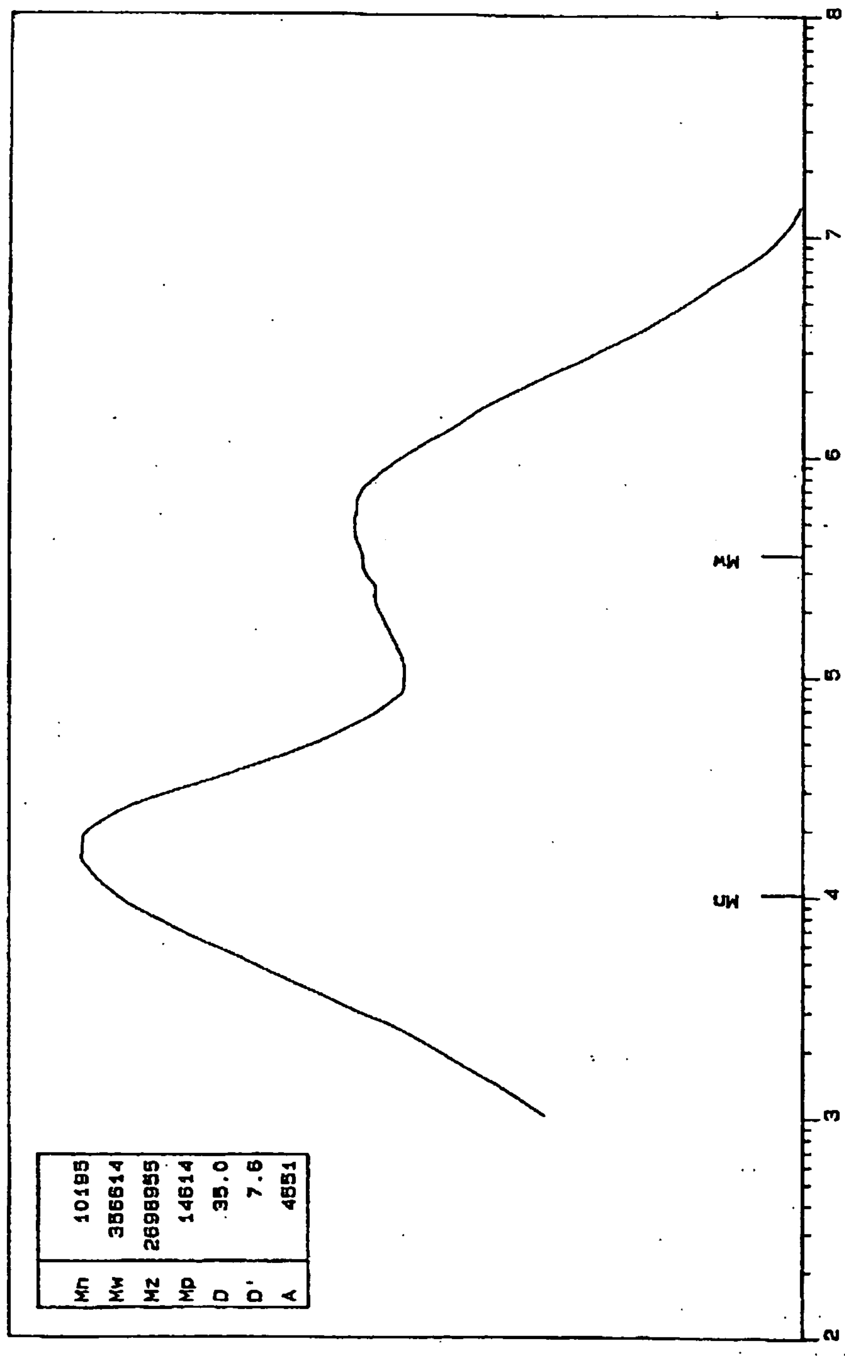
6
7
8

FIG.3


Mn 10185
Mw 356614
Mz 2698955
Mp 14614
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D' 7.6
A 4551
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Mw
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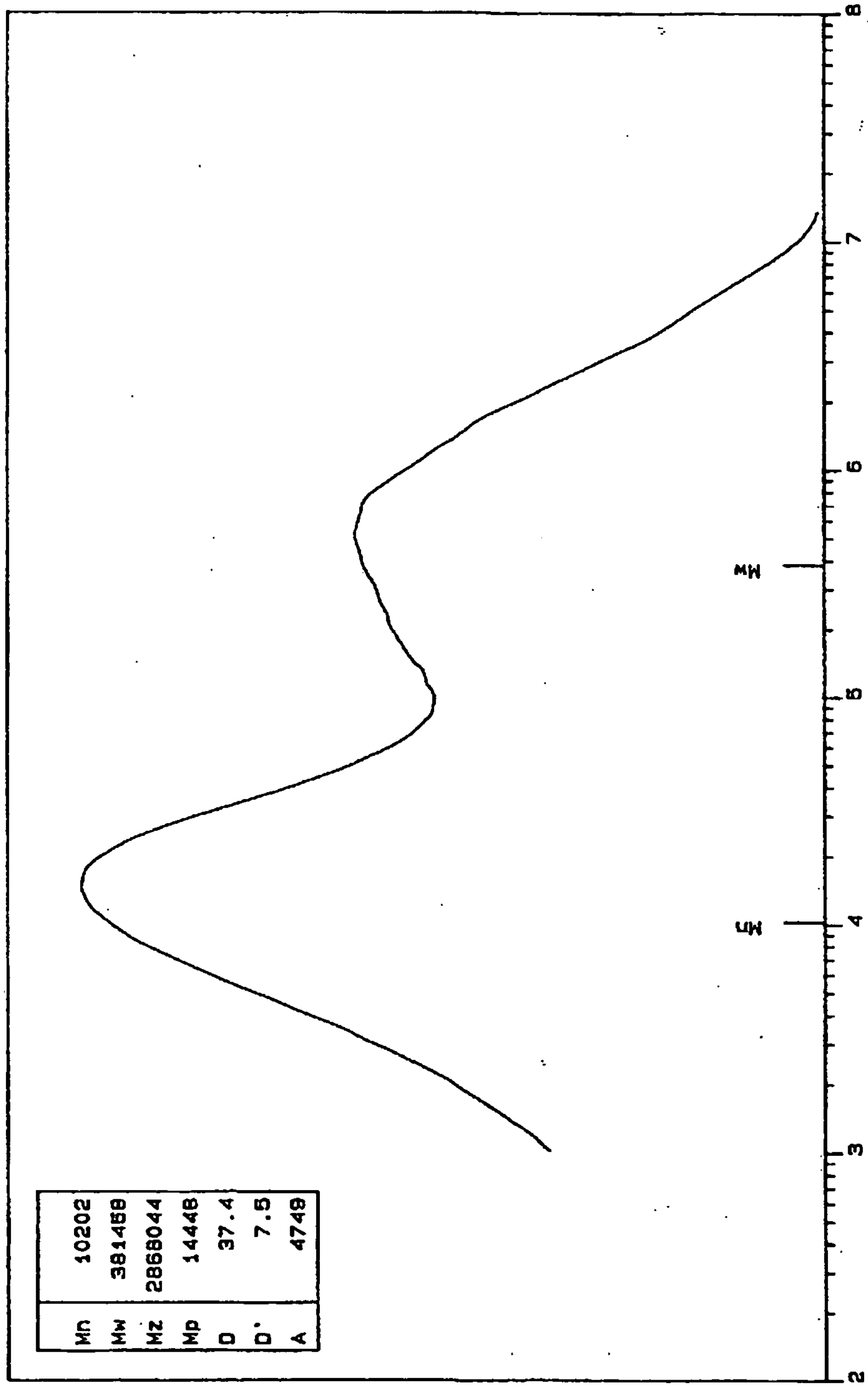
6
7
8

FIG.4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Mw 381458
Mz 2868044
Mp 14448
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D' 7.5
A 4749
Mn
Mw
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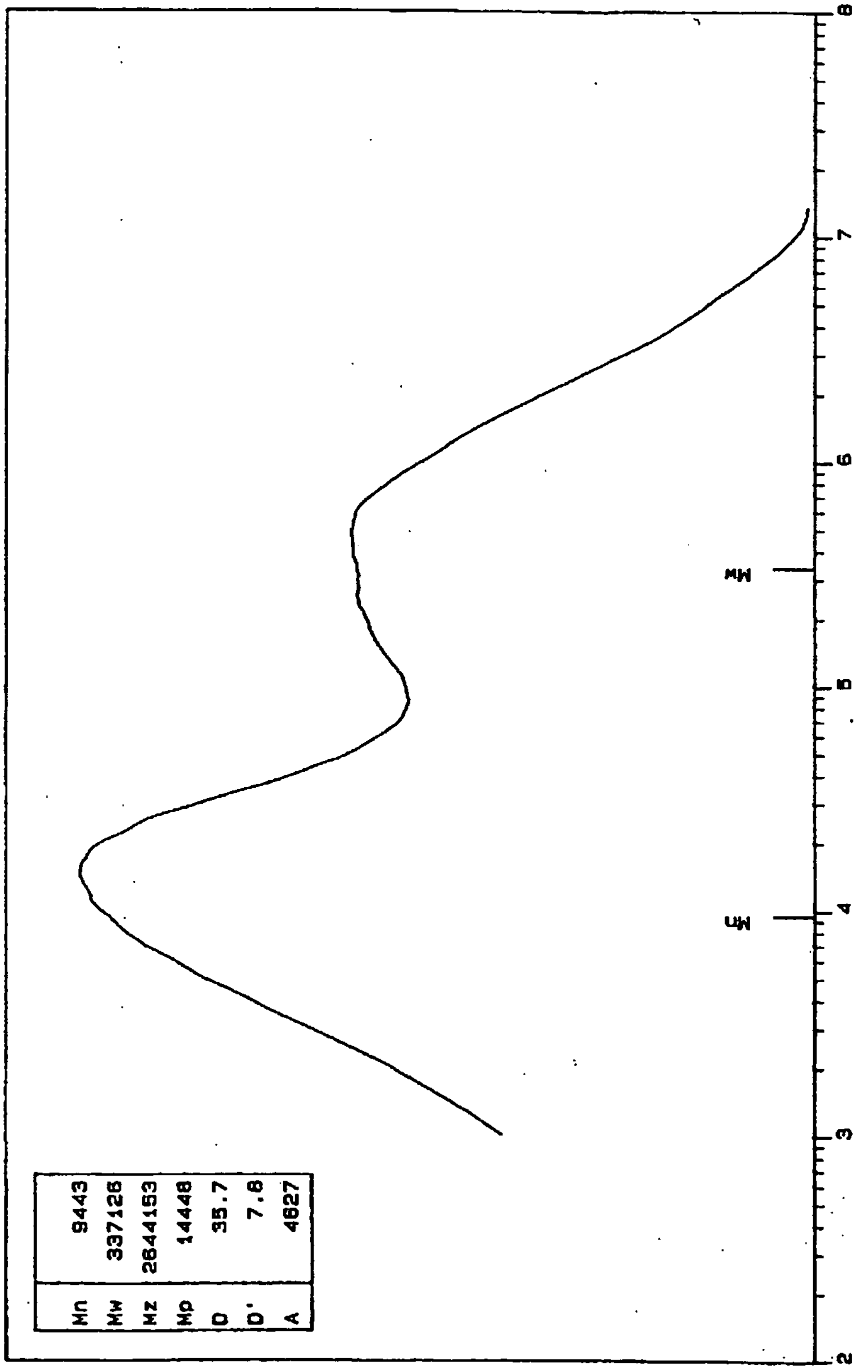
6
7
8

FIG.5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Mw 337126
Mz 2644153
Mp 14448
D 35.7
D' 7.8
A 4627
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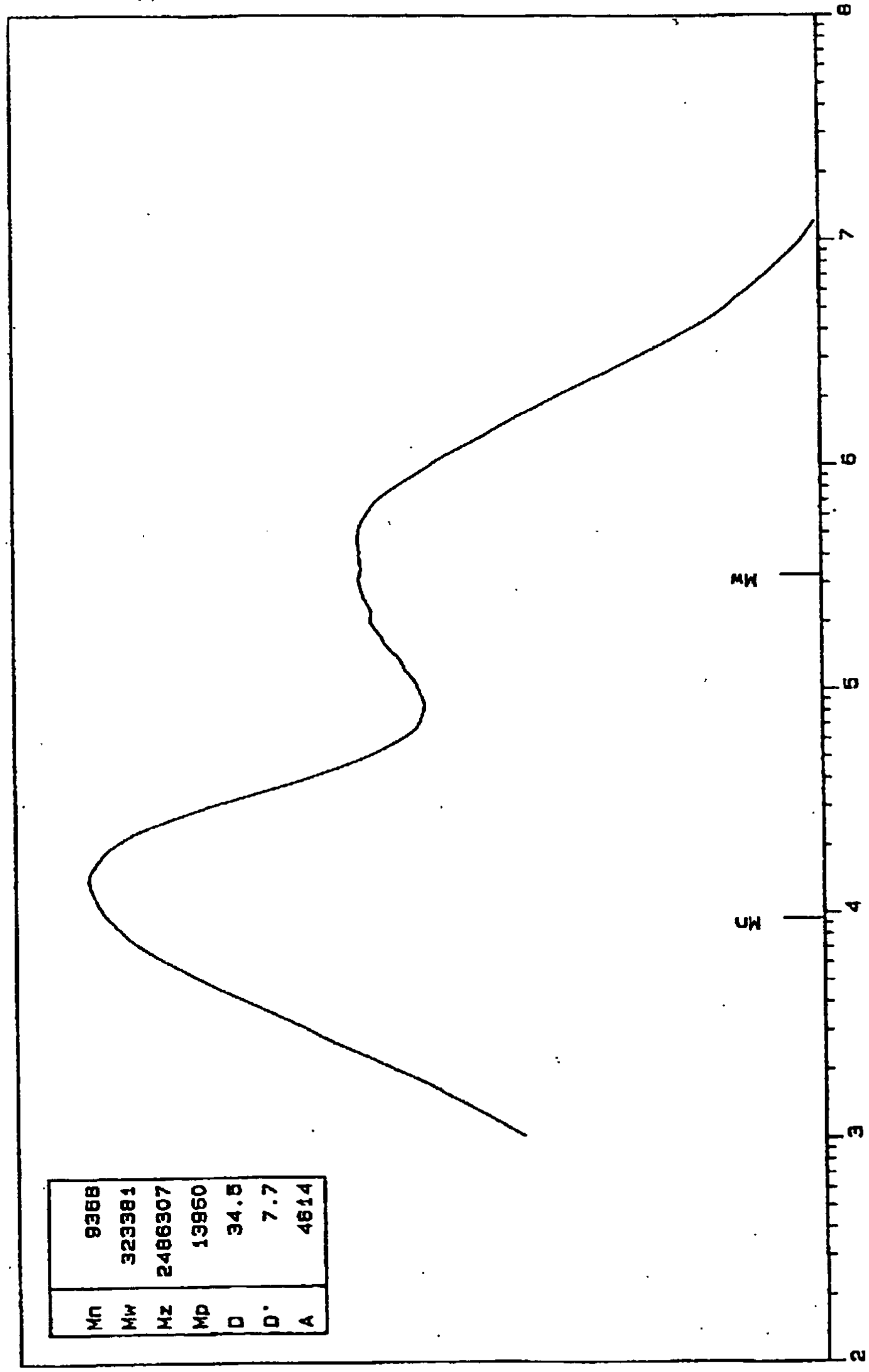
7
8
Mn
Mw

FIG.6


Mn 9368
Mw 323381
Mz 2486307
Mp 13960
D 34.5
D' 7.7
A 4614
Mn
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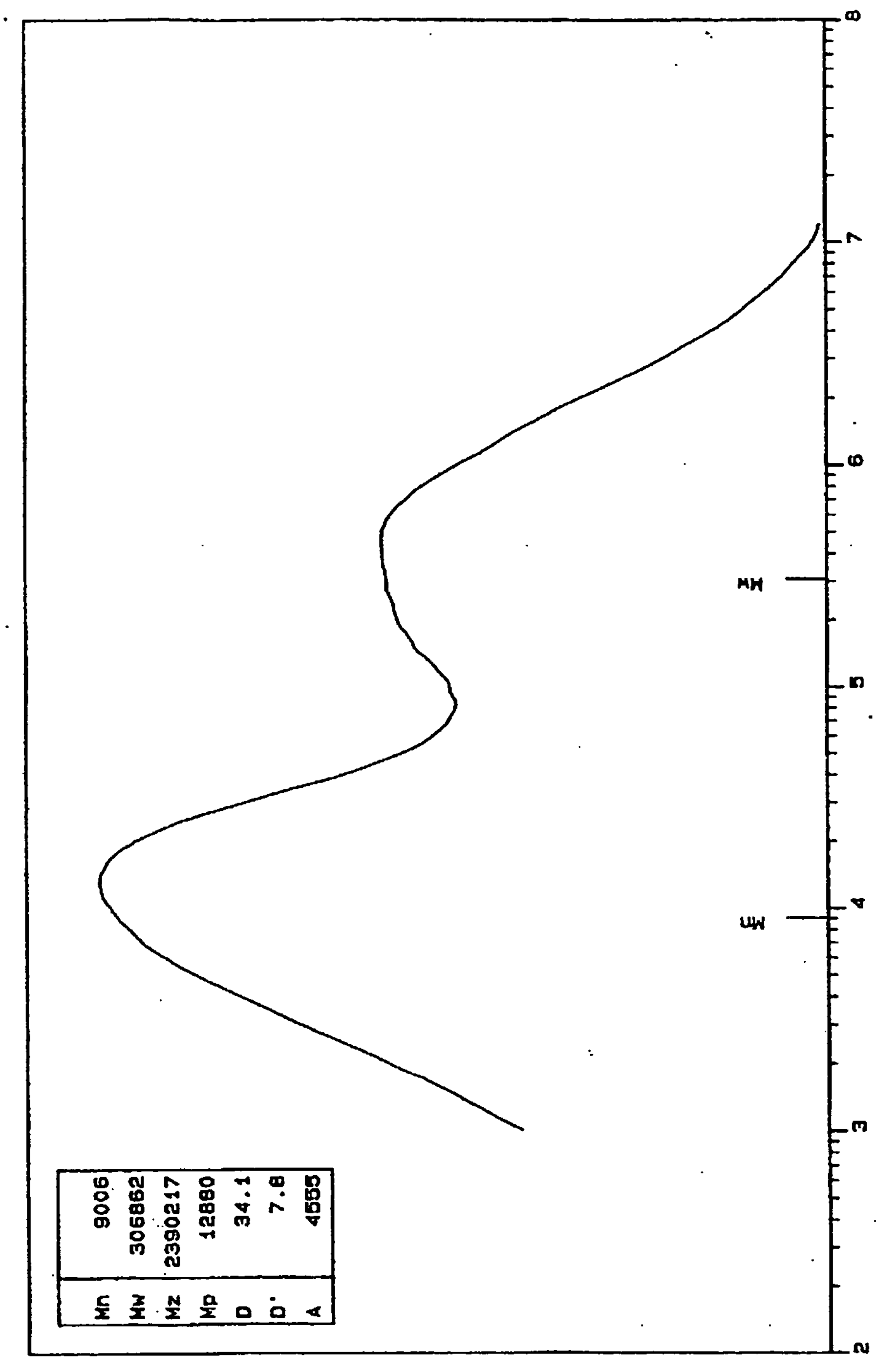
4
5
6
7
8

FIG.7


Mn 9006
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Mz 2390217
Mp 12880
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D' 7.8
A 4555
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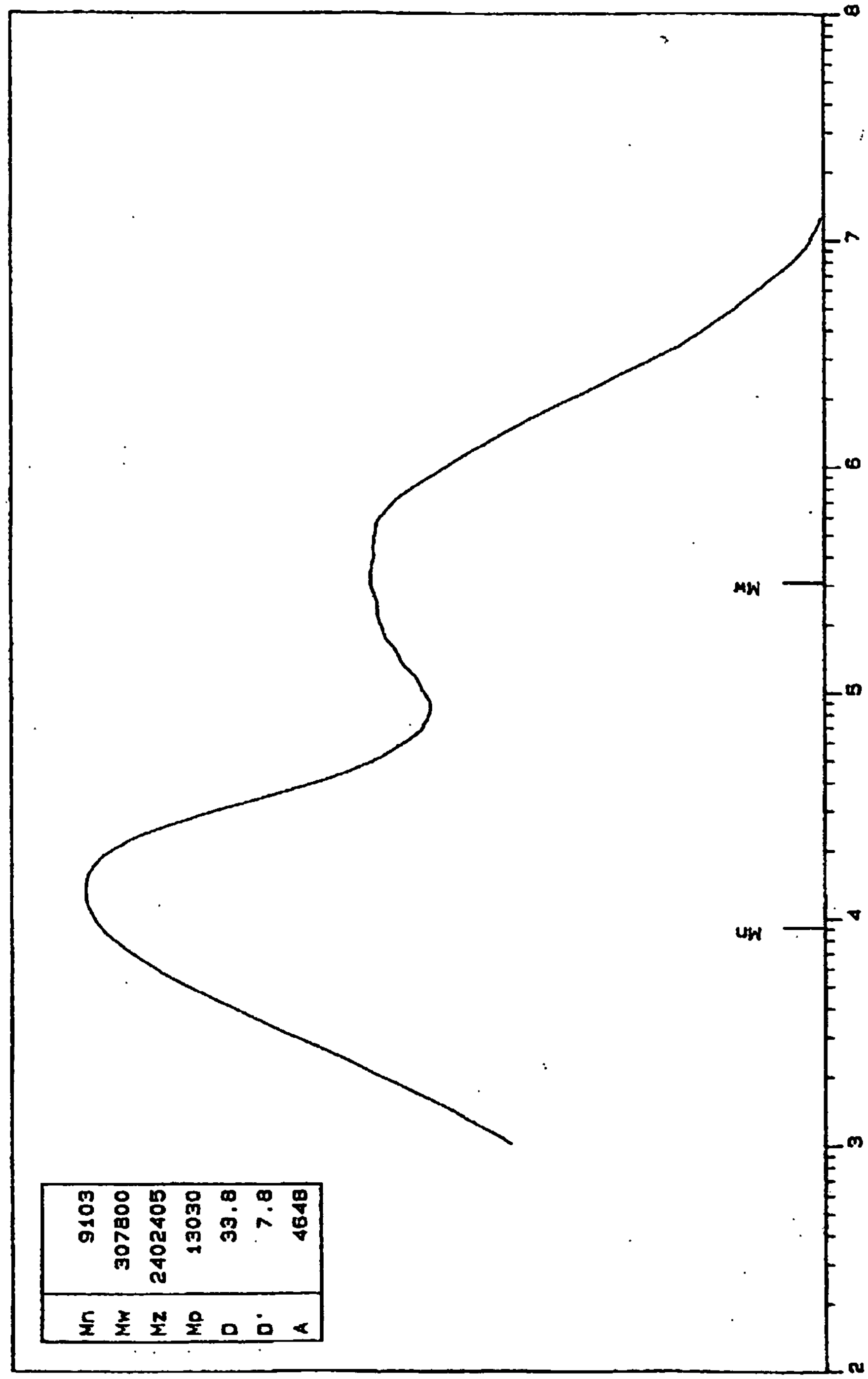
6
7
8

FIG.8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Mw 307800
Mz 2402405
Mp 13030
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A 4648
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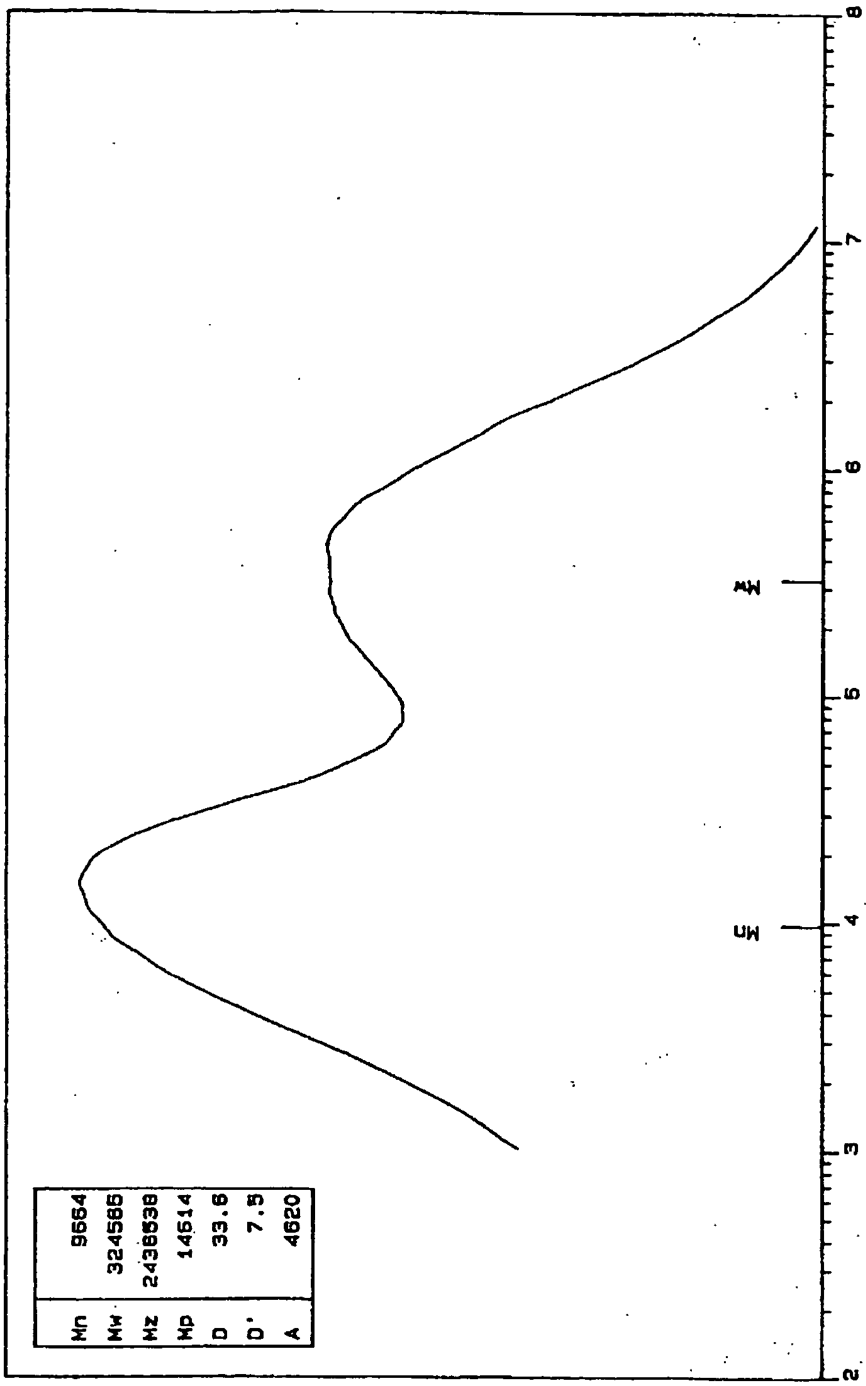
6
7
8

FIG.9


Mn 9564
Mw 324585
Mz 2438538
Mp 14514
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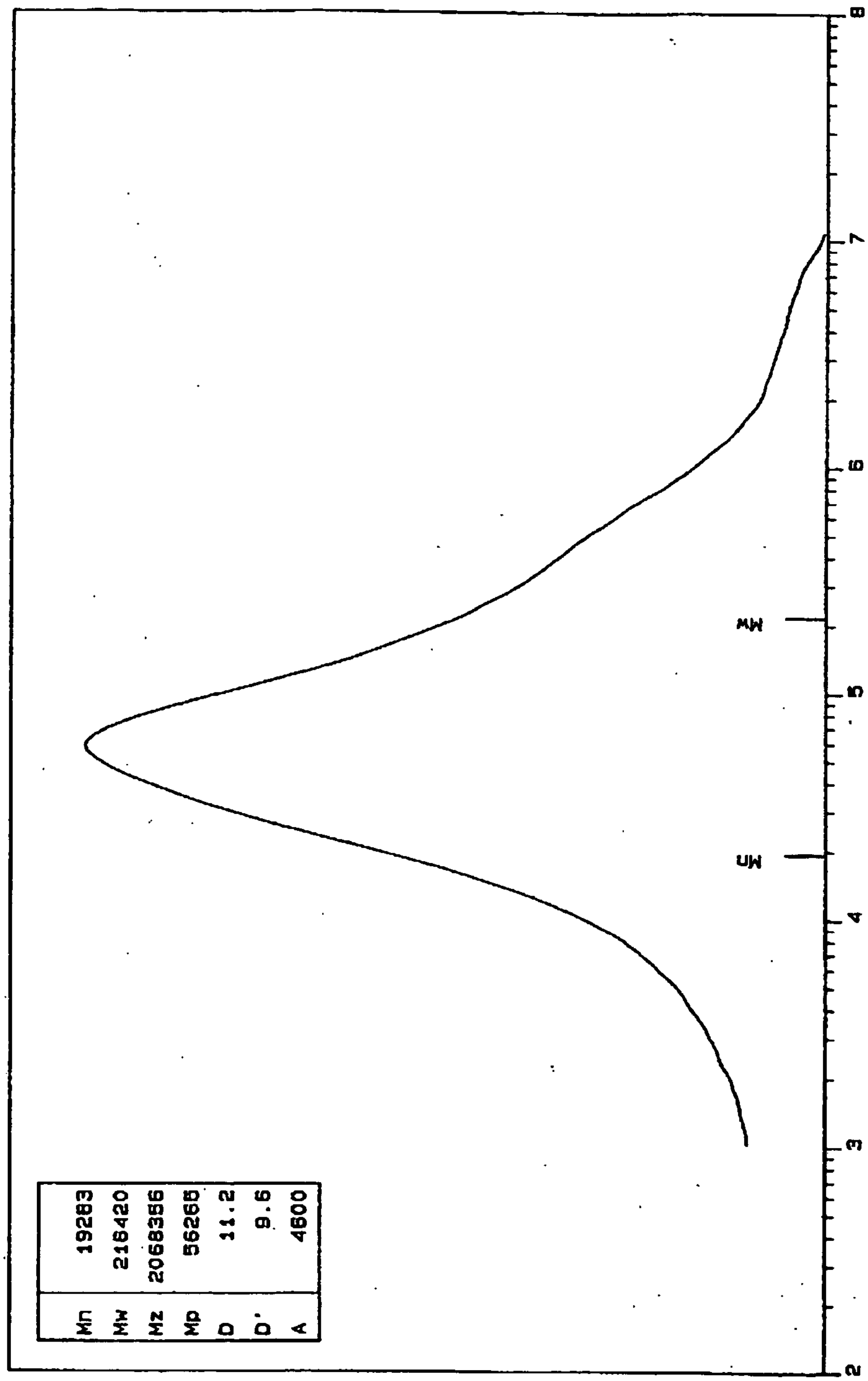
6
7
8

FIG.10


Mn 19283
Mw 216420
Mz 2068356
Mp 56265
D 11.2
D' 9.6
A 4600
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Mw
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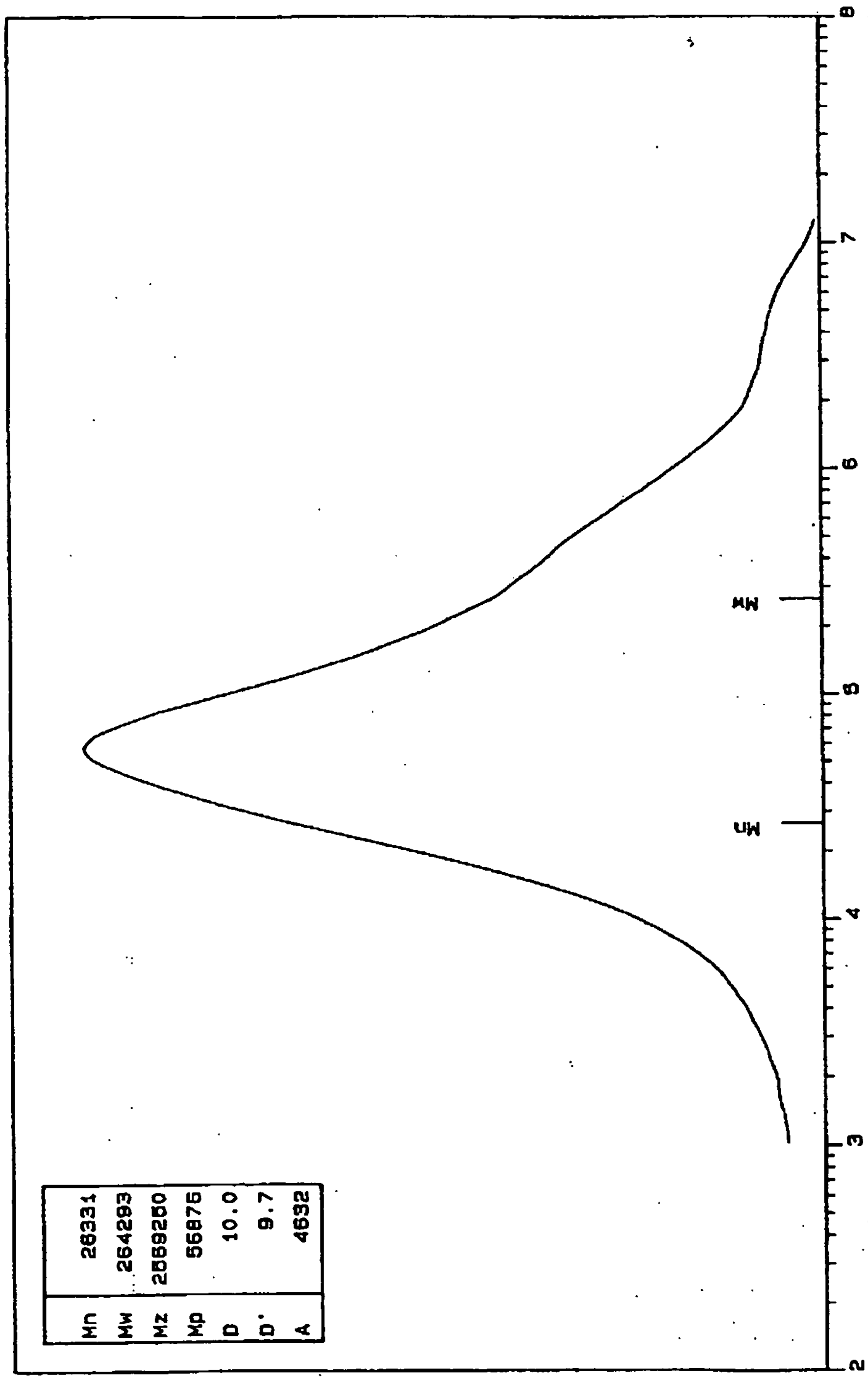
6
7
8

FIG.11


Mn 26331
Mw 264293
Mz 2669250
Mp 56876
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A 4632
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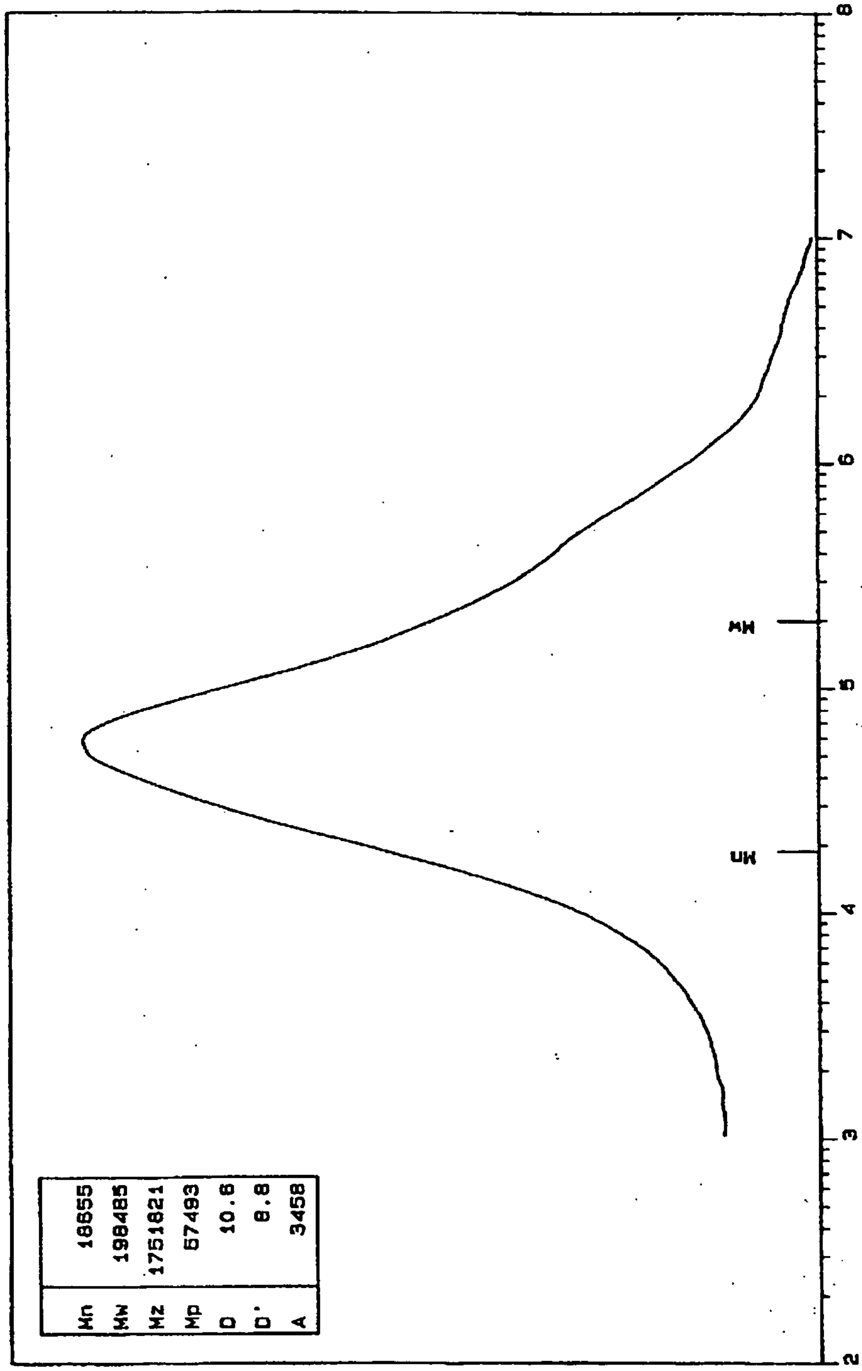
6
7
8

FIG.12


Mn 18655
Mw 198485
Mz 1751821
Mp 57493
D 10.6
D' 8.8
A 3458
Mn
Mw
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6
7
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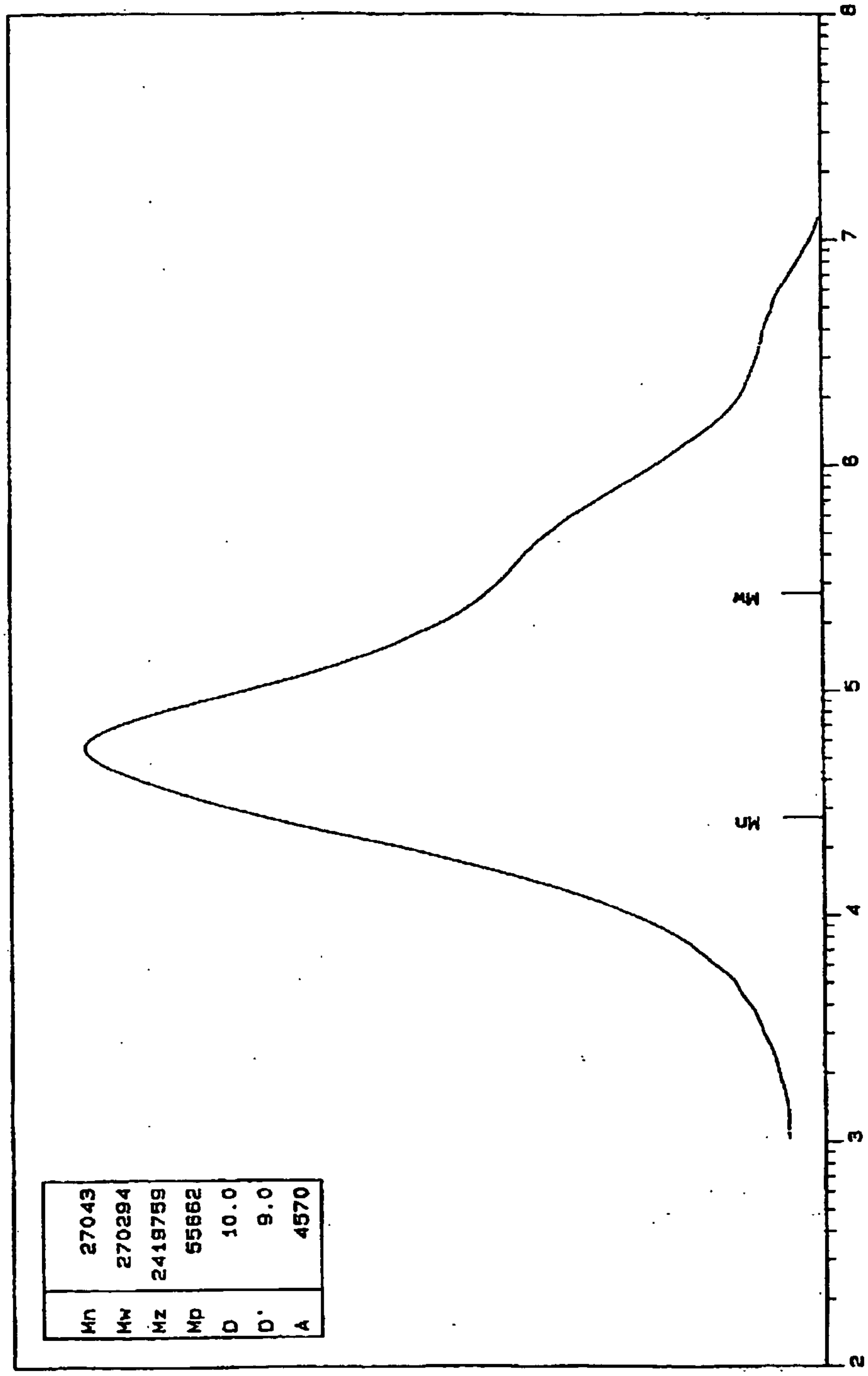
FIG.13


Mn 27043
Mw 270294
Mz 2418759
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D' 9.0
A 4570
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7
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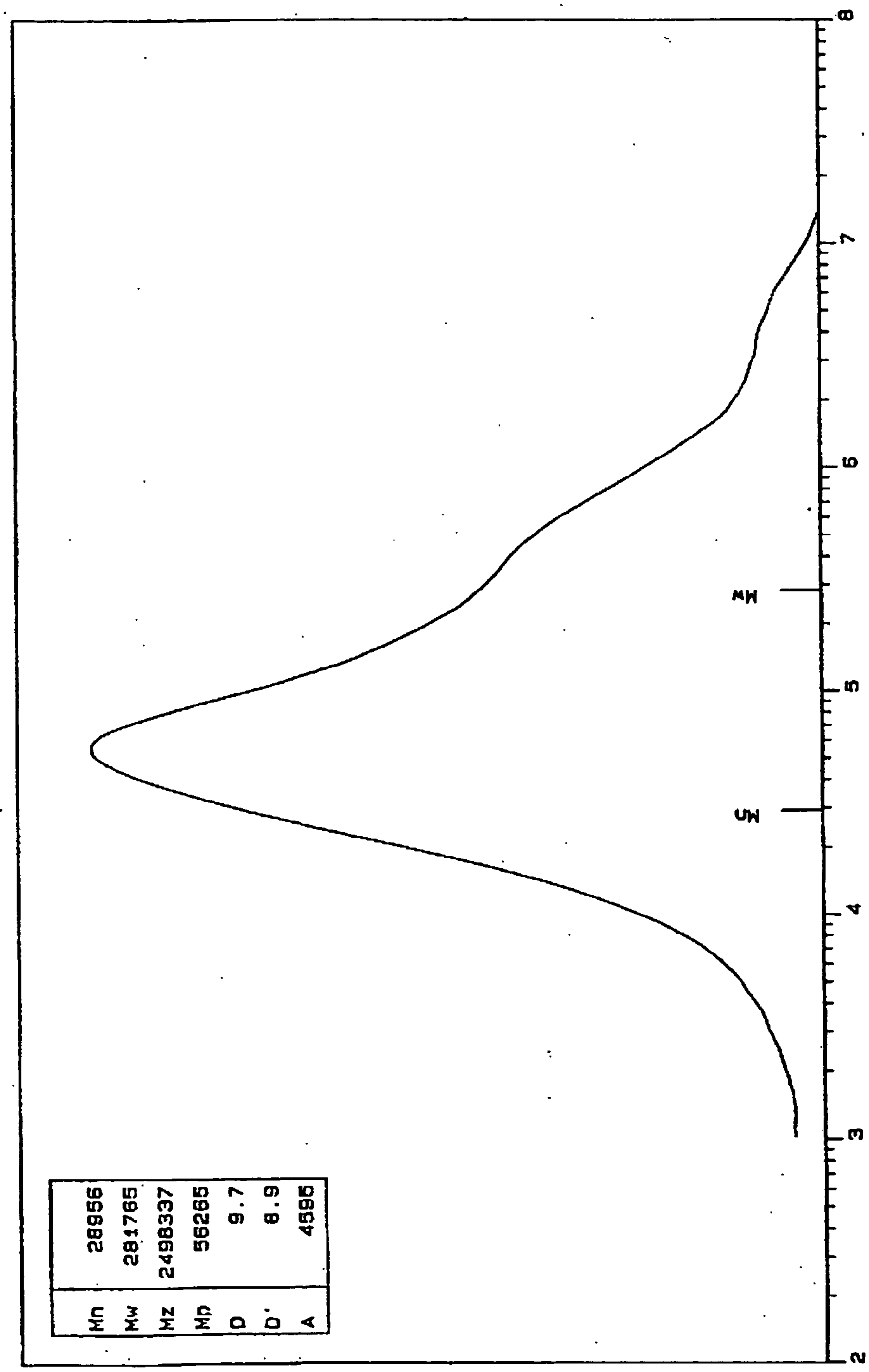
FIG.14



Mn 28956
Mw 281765
Mz 2498337
Mp 56265
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D' 8.9
A 4595
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Mz
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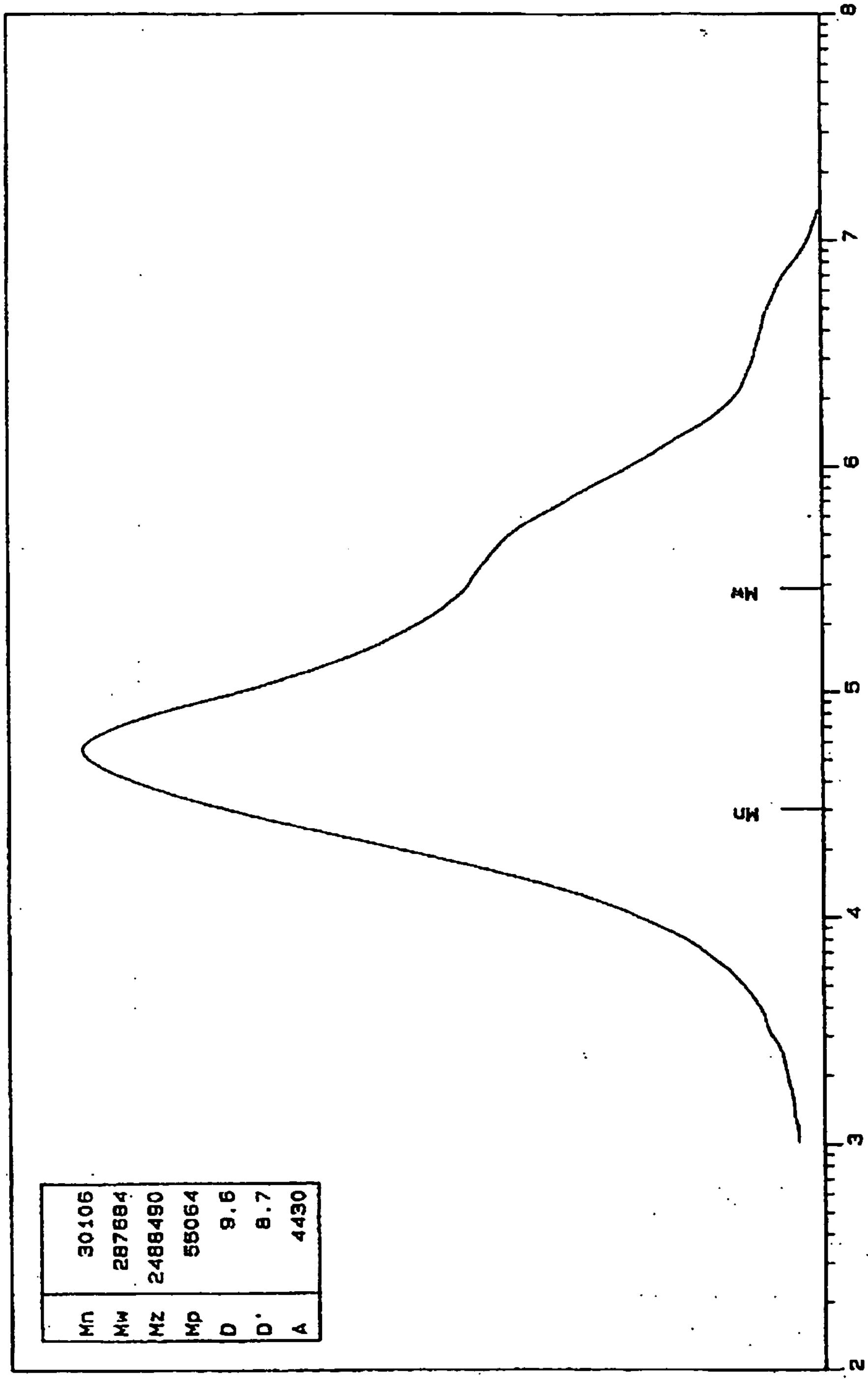
FIG.15


Mn 30106
Mw 287684
Mz 2488490
Mp 55064
D 9.6
D' 8.7
A 4430
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Mw
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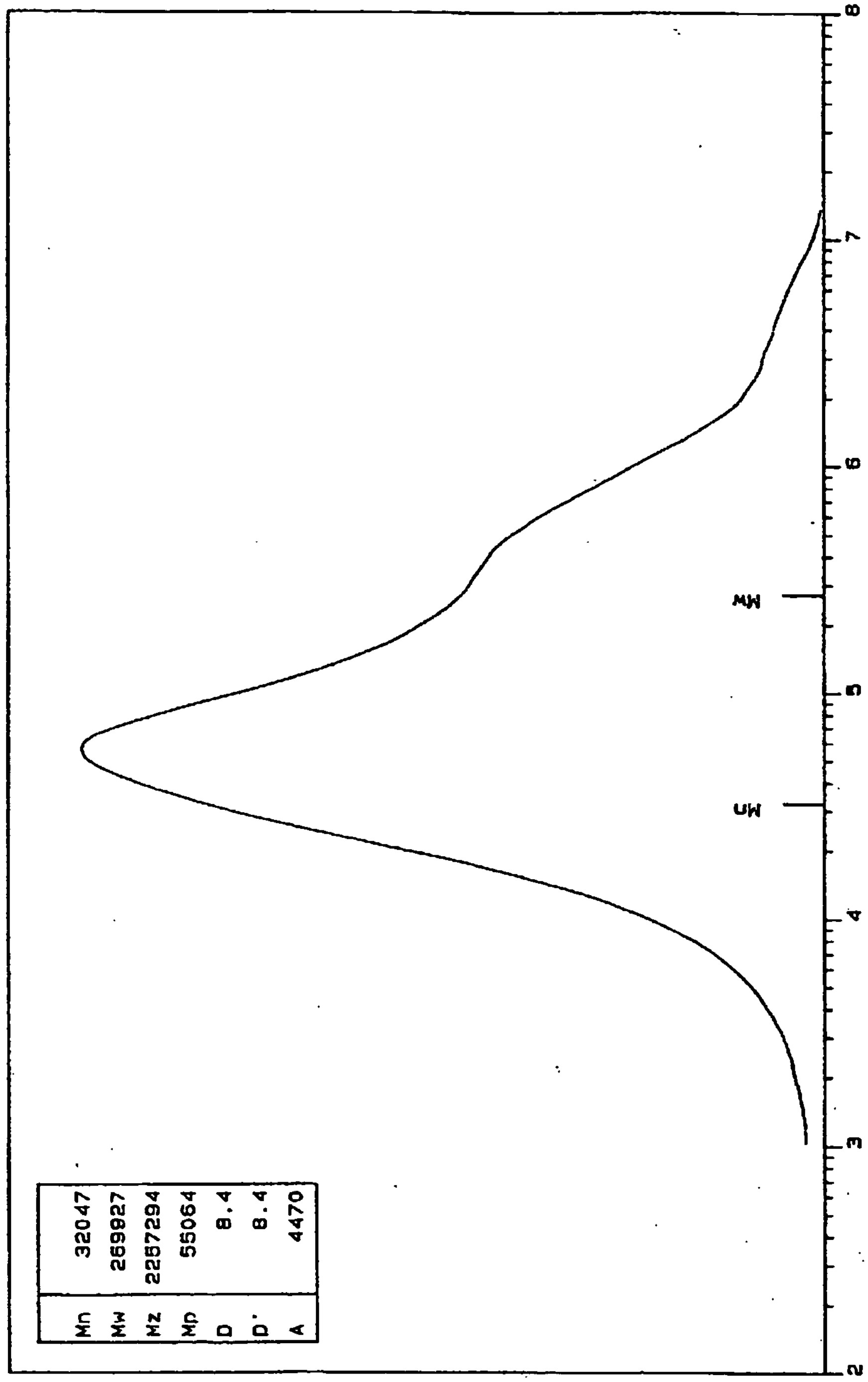
FIG.16


Mn 32047
Mw 269927
Mz 2257294
Mp 55064
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A 4470
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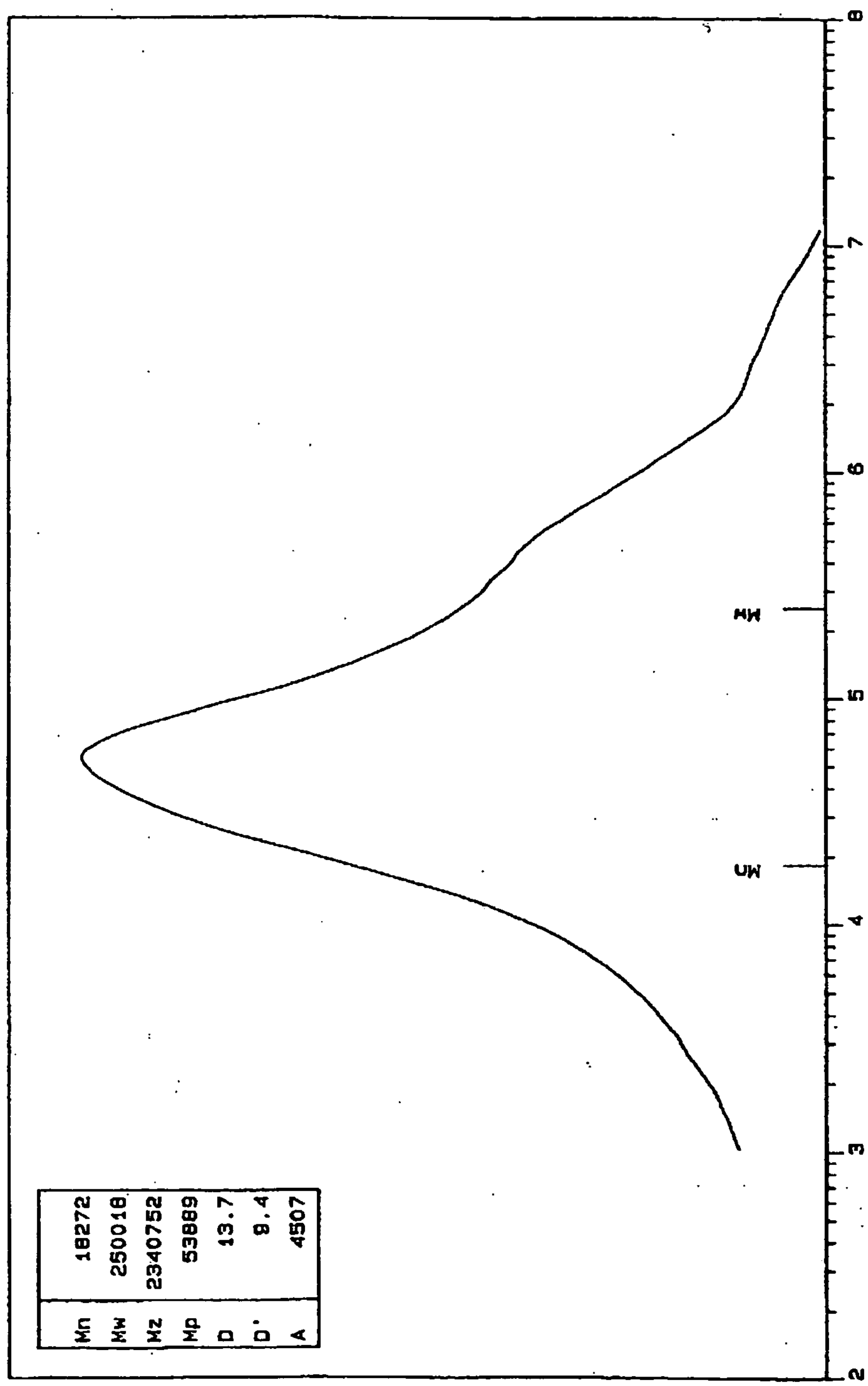
FIG.17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Mw 250018
Mz 2340752
Mp 53889
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D' 9.4
A 4507
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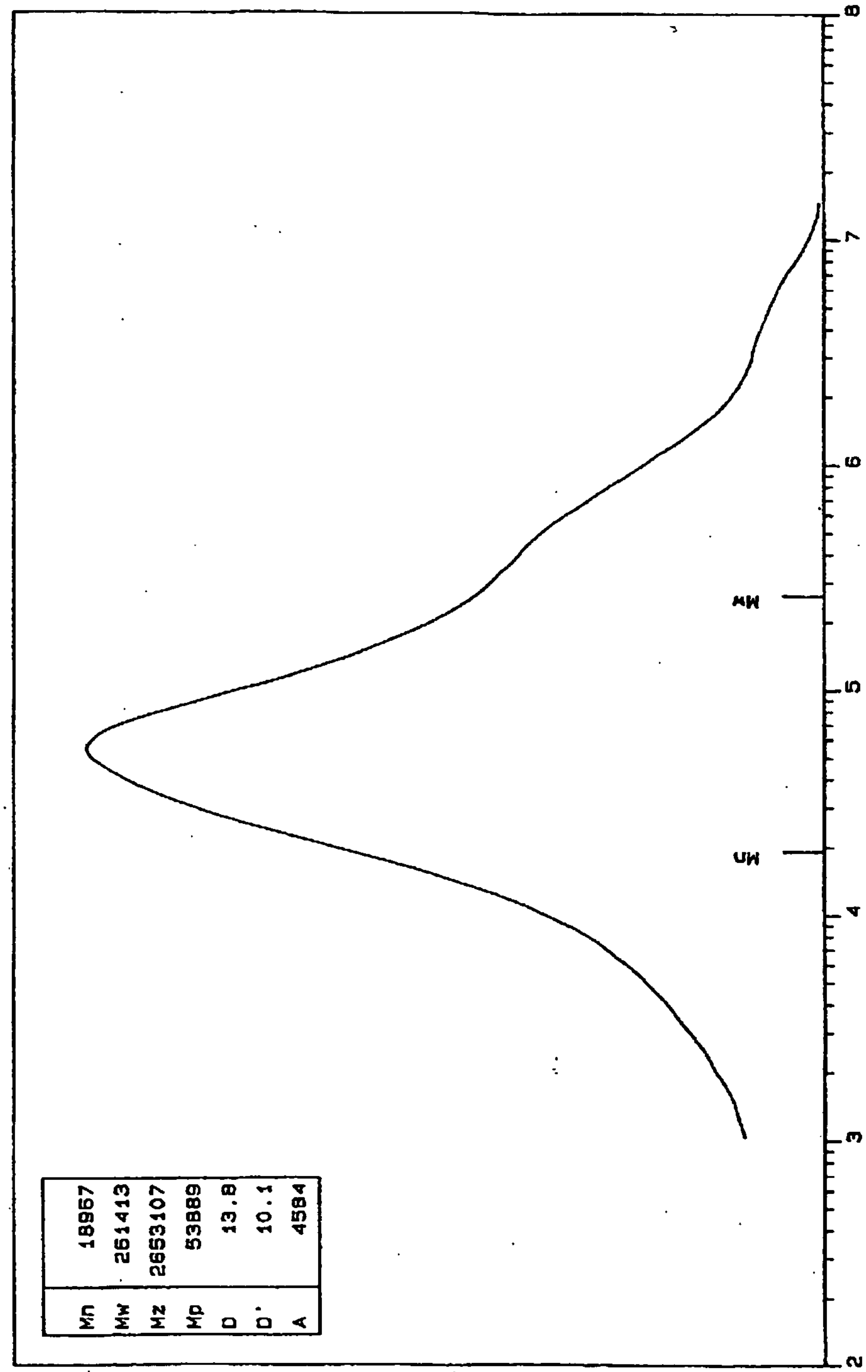
FIG.18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Mz 2653107
Mp 53889
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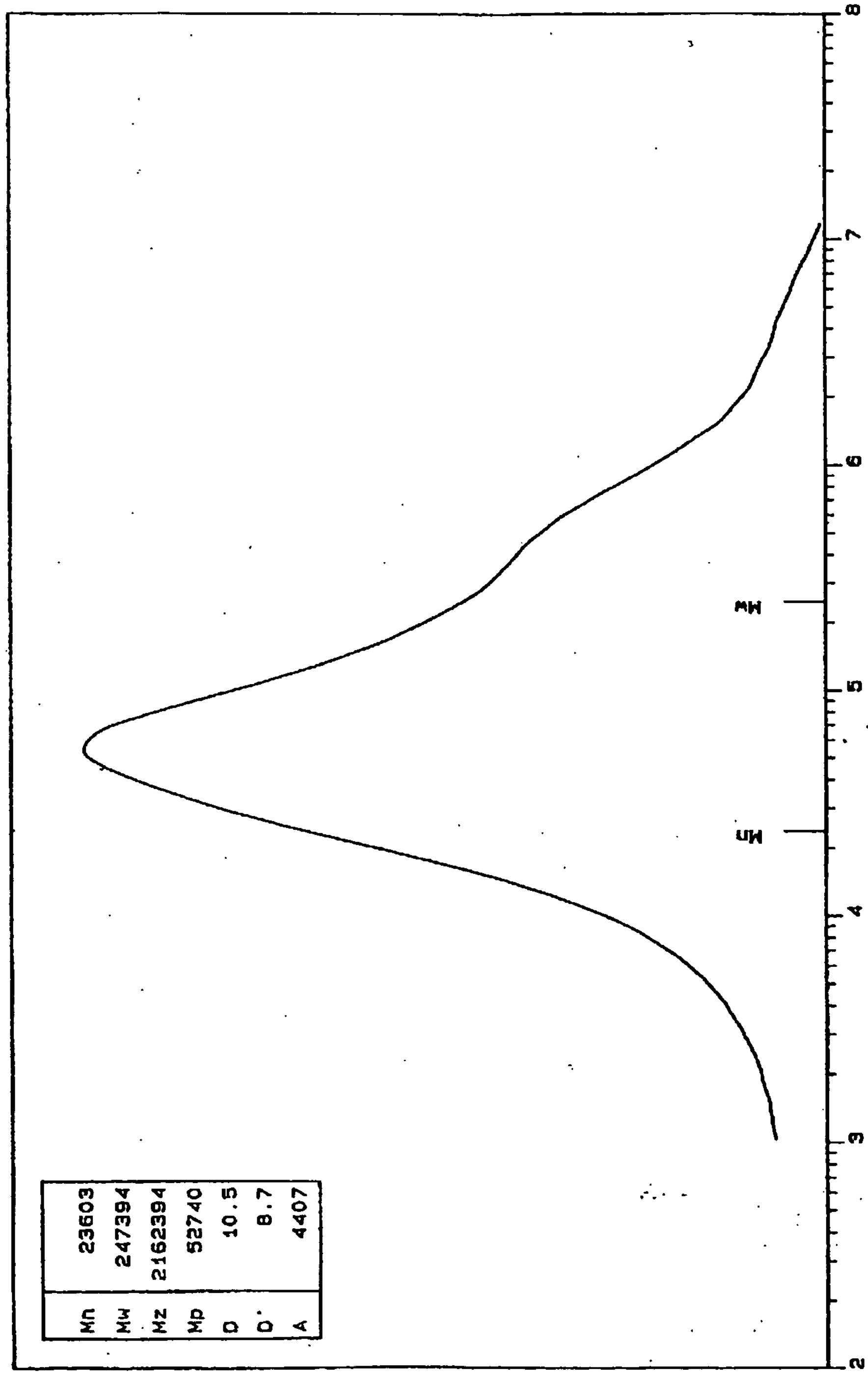
FIG.19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Mw 247394
Mz 2162394
Mp 52740
D 10.5
D' 8.7
A 4407
Mn
Mw
2
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FIG.20

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 93 87 0064

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 452 920 (MITSUI PETROCHEMICAL INDUSTRIES LTD.) * example 13 * ---	1-15	C08F4/602 C08F10/00
A	US-A-4 659 685 (W.M.COLEMAN III) * abstract * -----	15	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C08F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	16 SEPTEMBER 1993	Marco Serravalle

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
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E : earlier patent document, but published on, or after the filing date
D : document cited in the application
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